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# Sildenafil drug as a safe anticorrosion for 6063 aluminum alloy in acidic and alkaline solutions: Theoretical and experimental studies



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## ABSTRACT

The corrosion inhibition of aluminum alloy surface (6063AA) by Sildenafil (SIL) in 1 M for both HCl and NaOH solutions was investigated using weight loss, electrochemical techniques and quantum calculations. The inhibitory effect of SIL was explained by the formation of the complex adsorbed on the 6063AA surface. The adsorption obeyed Langmuir isotherm. The adsorption of the SIL is a mix of physical and chemical adsorption, where the free energy of adsorption was found to equal  $-39.12$  and  $-34.6$  KJ/mol, in HCl and NaOH, respectively. Experimental outcomes showed that SIL significantly inhibits the dissolution of 6063Al in both acidic and alkaline media. SIL drug acts as a mixed inhibitor in both two aggressive solutions. The correlation of the inhibition performance of SIL on 6063Al with the molecular structure was adopted using Dmol3 (Materials Studio v7. 0) based on some descriptors as  $E_{\text{HOMO}}$  and  $E_{\text{LUMO}}$ . Fukui indices were computed to determine the active sites of the inhibitor molecules. The equilibrium adsorption behavior of SIL on Al (1 1 1) surface was examined using molecular dynamics simulation. The quantum chemical descriptors were found suitable in explaining the inhibitive action of SIL.

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## 1. Introduction

Aluminum is not costly metal and has excellent properties [1–3]. It has wide range of industrial applications, as for instance, aerospace and electronics. The wide applications of Al demand its use in various environments containing acids, alkali and salt solutions and thus subjected to corrosive attacks [4]. Also, the pickling of Al and the electrochemical etching are achieved in hydrochloric acid solutions, and this leads to a substantial dissolution of Al due to corrosion which is an inevitable problem [5]. The literature contains several approaches to protect Al from the corrosion attack, and among these approaches, using organic molecules are considered as one of the most efficacious solutions to the corrosion problem [6–17]. These inhibitors exert their action via adsorption, which is influenced by several factors such as the elec-

tron density at the donor site and the polarizability of the functional group. There are many limitations to the use of organic compounds as a corrosion inhibitor. Among these limitations, poor biodegradability and toxicity are considered as the main problems to be overcome. Recently, the natural products of plant origin or drugs have been examined as corrosion inhibitors as they are eco-friendly. Several merits are fulfilled in some drugs and thus they are considered as a candidate corrosion inhibitors; some of these merits are: (a) the drugs are mainly soluble in the aqueous media, (b) the drug molecules contain hetero atoms acting as the active centers because of their high adsorption affinity, (c) the drugs are reported to be environmentally benign in biological systems and (d) can be easily manufactured and purified [18–24]. Now, the research is directed to the area of ecofriendly corrosion inhibitors including plant extract and other safe inhibitors [25–28]. In the current work, the use of sildenafil drug (SIL) as a corrosion inhibitor of aluminum alloy (6063AA) in both acidic and alkaline media is examined at various temperatures using chemical and electrochemical methods. The mode of exerting of this drug its inhibition action is evaluated via studying its adsorption mode as well as

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kinetics and thermodynamic parameters. In addition, the experimental results are sustained by theoretical calculations.

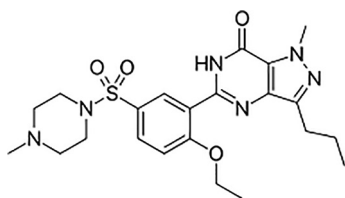
## 2. Materials and methods

### 2.1. Aluminum sample

Aluminum alloy (6063AA) is the sample to be protected from corrosion. The chemical composition of this in weight % 0.42 Si, 0.17 Fe, 0.001 Cu, 0.009 Mn, 0.42 Mg, 0.001 Ni, 0.01 Ti, 0.001 Zn, 0.0012 Na and the balance is Al. The working electrodes of Al in weight loss tests are in form of coupons of dimension  $1 \times 3 \times 0.2 \text{ cm}^3$ , while in electrochemical tests were in the form of rod with exposed surface area of  $0.452 \text{ cm}^2$

### 2.2. Inhibitor

The chemical composition of sildenafil (SIL) which is used as an anticorrosive for corrosion of 6063 AA is as follows [29];



### 2.3. Solutions

Bidistilled water was utilized for preparing the examined solutions of (HCl) which is of AR. For weight loss and electrochemical measurements, a 50 ml electrolyte solution for was used. The concentration range of inhibitors employed was  $5 \mu\text{M}$  to  $0.5 \text{ mM}$ . Solutions of  $1.0 \text{ M}$  NaOH were prepared by weighing the appropriate amount and dissolving in the suitable volume, and then the concentration was determined volumetrically.

### 2.4. Weight Loss (WL) measurements

The samples, after being pretreated with emery paper were subjected to weight loss in acid and alkaline media both in the absence and presence of SIL drug. The inundation time for weight loss was over a time period at a certain temperature. WL measurements were made as described earlier [30]. To ensure accuracy of the results, three parallel trials experiments were performed with precision, and average weight loss was estimated.

### 2.5. Potentiodynamic polarization (PP) method

PP experiments were conducted in a conventional corrosion cell of three electrodes, i.e. platinum spiral wire as an auxiliary electrode, a saturated calomel anode (SCE) and working electrode (fabricated from aluminum alloy, with the exposed surface area ( $0.452 \text{ cm}^2$ )). Before any test the electrode surface has been treated as cited above. Before starting the measurements, the steady potential was attained, it takes ca. 30 min. Measurements were conducted with an Autolab PGSTAT 20 Potentiostat (Ecochemie, Utrecht Netherlands) driven by GPES 4.4 Software. Both anodic and cathodic PP curves were recorded for the uninhibited and inhibited solution and further analyzed for extracting various corrosion parameters. Measurements were performed at a sweep rate

of  $2 \text{ mV/s}$ . Corrosion current density values were obtained from the extrapolation of the linear Tafel segments of anodic and cathodic curves.

### 2.6. Electrochemical impedance spectroscopy (EIS) studies

EIS was achieved utilizing AC signs of  $5 \text{ mV}$  peak to peak amplitude, then fitted utilizing the Echem Analyst (Gamry) programmer to proper proportional circuit. Then results were tested by using of the equivalent circuit. The percentage inhibition efficiency (% IE) of the examined inhibitor were estimated using the above three techniques, i.e., weight loss, polarization and impedance techniques using the following equation:

$$\%IE = \left[ 1 - \frac{A}{B} \right] 100 \quad (1)$$

The surface coverage ( $\theta$ ) was computed as follows: ( $\theta = \%IE/100$ ) where A and B denotes the weight loss or the corrosion current density in case of WL and PP techniques in the presence of sildenafil drug and in the blank solutions, respectively. In the case of EIS technique, A and B refer to the charge transfer resistances in the absence and presence of SIL drug, respectively.

## 3. Results and discussion

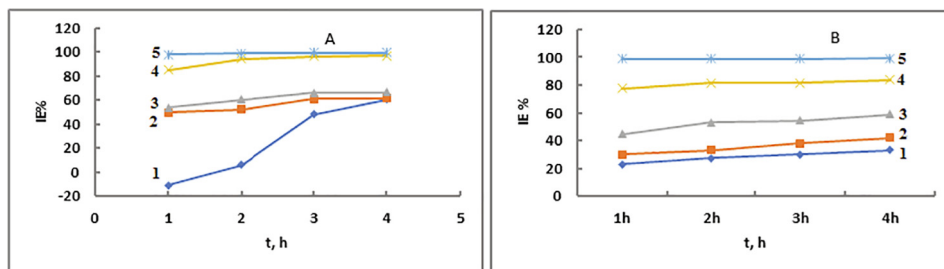
### 3.1. WL methods

Fig. 1(A & B) illustrates the change of the % IE with the inundation time at  $297 \text{ K}$  for Al in  $1 \text{ M}$  for both HCl and NaOH solutions, in the free and with diverse concentrations of SIL drug. It is obvious that, the increase in the SIL concentration reduces the corrosion rate and hence increases the % IE. A comparison of the results obtained in acid and alkaline medium reveals several interesting points.

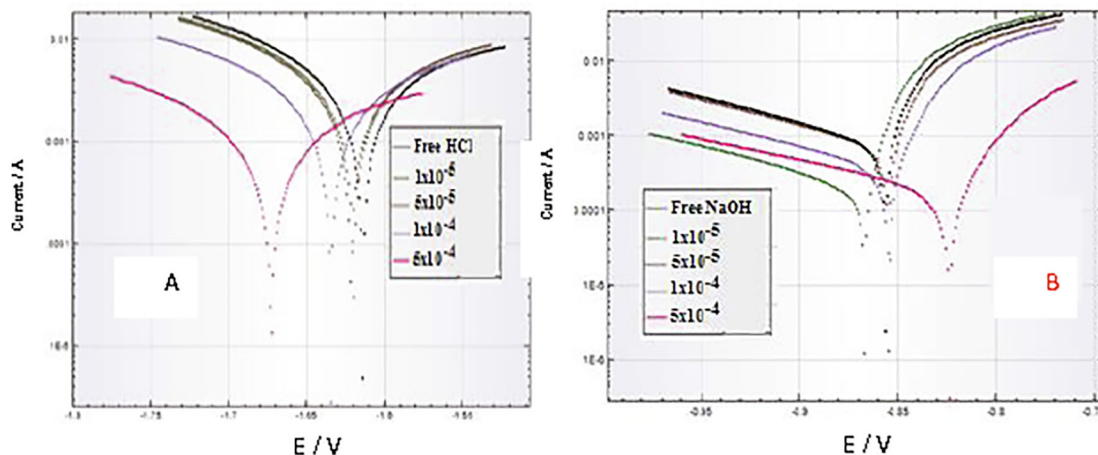
1. The inundation time is significant in the case of acidic medium; it takes at least 2 h for the inhibitor concentration in the range  $5$  to  $100 \mu\text{M}$  to achieve the largest possible inhibition efficiency at the nominated concentration. In contrary, in alkaline medium, the greatest possible inhibition efficiency is attained in all studied concentrations at shorter time of 1 h (the smallest time examined). This indicates that the inhibitor performance in alkaline medium is more efficient than in acid. It is likely that the nitrogen atoms' lone pair might not be completely available in acid medium as much as in alkaline medium because in the former one it is likely that the nitrogen atom is protonated.

The increase of the % IE with the inundation time reflects the constructing of the protection film, and that a synergistic effect is acquired with the passive film formed on 6063AA in alkaline medium [31].

2. In acid medium, at some concentrations, the % IE decreases slightly at larger time pointing to some desorption of the SIL. Similar observations have been reported to inhibit aluminum corrosion in alkaline and acidic media using plant extracts [32–35].
3. The time needed for attaining the greatest possible inhibition efficiency depends on the concentration of SIL drug; it decreases with increasing the inhibitor concentration
4. As concentration increases the % IE increases in both studied media, reaches near 100%, indicating the highest efficiency of the studied SIL drug under the present conditions.



**Fig. 1.** The relation between the % IE and time at various concentrations of SIL drug for 6063 AA in A) 1.0 M HCl B) 1.0 M NaOH solutions containing 1)  $5 \times 10^{-6}$  M SIL 2)  $1 \times 10^{-5}$  M SIL 3)  $5 \times 10^{-5}$  M SIL 4)  $1 \times 10^{-4}$  M SIL and 5)  $5 \times 10^{-4}$  M SIL.



**Fig. 2.** (A) PP curves of 6063AA in free A) 1.0 M HCl B) 1.0 M NaOH solutions containing various concentrations of SIL:  $5 \times 10^{-6}$  M SIL 2)  $1 \times 10^{-5}$  M 3)  $5 \times 10^{-5}$  M 4)  $1 \times 10^{-4}$  M 5)  $5 \times 10^{-4}$  M.

3.2. PP measurements

Fig. 2A and B demonstrate PP measurements of the 6063 AA electrode in both media in the absence and presence of SIL. Several parameters such as corrosion potential ( $E_{corr}$ ), corrosion current density ( $I_{corr}$ ), anodic ( $b_a$ ) and cathodic ( $b_c$ ) slopes extracted from these figures are tabulated in Table 1. Inspection of this figure reveals the following points, upon increasing the concentration of EIS;

- i. Both the dissolution of Al and cathodic reactions are impeded, albeit to different extents. In the case of NaOH the cathodic reaction is more impeded. In contrary, in HCl, the anodic one is more retarded.
- ii.  $E_{corr}$  positively shifted in HCl, and this indicates that the effect on the anodic process is significant, comparatively. In sodium hydroxide, the corrosion potential is shifted negatively. This indicates that the effect on the cathodic process

is greater in this case. This might be due to the different charge density on the SIL molecule (c.f. quantum calculations). However, the shift is not significant to nominate the inhibitor if it is anodic or cathodic one [36,37].

- iii. The  $I_{corr}$  values decrease significantly with increasing SIL concentration and consequently the %IE increases indicating the inhibiting action of this drug is significant under the current conditions. It reaches ca. 93.63% in 1.0 M HCl, and 90.59% in 1 M NaOH solutions. The obtained inhibition efficiency is in consistent with those shown above using WL. Regarding the Tafel slopes, the nominal values obtained in the absence and presence of SIL are not significantly different, points to the simple adsorption of SIL on the electrode.

3.3. EIS studies

The inhibitory vigor of SIL towards the dissolution 6063 AA was also verified by EIS studies in both HCl and NaOH solutions and

**Table 1**  
Corrosion parameters obtained from corrosion of AA in free 1.0 M HCl and 1.0 M NaOH solutions containing various concentrations of SIL drug using PP and EIS methods.

Conc., M	$-E_{corr}$ mV	$\beta_a$ mV/decade	$-B_c$ mV/decade	$I$ mA/cm <sup>2</sup>	IE <sub>pp</sub> %	$R_{ct}(\Omega)$	IE <sub>EIS</sub> %
Free 1 M HCl	925.6	134	120	2.877	–	35.19	–
$1 \times 10^{-5}$ M	957.5	141	101	0.833	71.05	37.27	5.90
$5 \times 10^{-5}$ M	853.4	152	120	0.626	78.24	67.44	47.80
$1 \times 10^{-4}$ M	852.8	155	125	0.425	85.23	90.69	61.20
$5 \times 10^{-4}$ M	819.7	161	119	0.183	93.63	160.61	77.70
Free 1 M NaOH	1612.0	131	172	3.851	–	6.40	–
$1 \times 10^{-5}$ M	1618.0	131	156	1.811	52.97	8.20	21.95
$5 \times 10^{-5}$ M	1607.1	146	163	1.526	60.37	10.50	39.05
$1 \times 10^{-4}$ M	1616.2	144	162	0.734	80.94	22.50	71.55
$5 \times 10^{-4}$ M	1674.1	149	172	0.362	90.59	25.8	75.19

Nyquist plots are presented in Fig. 3. The polarization resistance ( $R_{ct}$ ) and the protection efficiency ( $IE_{EIS}\%$ ) values are given in Table 1. The spectra show depressed semicircles. This indicates a charge transfer controlled process [38,39]. The depression of the semicircles of the Nyquist denotes the inhomogeneity of the metal surface [40,41]. The spectrum obtained in HCl in the free and with some concentrations of EIS is characterized by one capacitive loop, while the spectrum obtained in NaOH is characterized by a three loops; two capacitive loops obtained at higher frequencies (HF) and lower (LF), separated by an inductive loop at intermediate frequencies (IF) [42]. Similar behavior has been reported for aluminum corrosion and its alloys in different solutions [43–46]. The capacitive loop obtained at higher frequency is probably attributed to a protective oxide film covering the metal surface. It corresponds to the oxidation of aluminum at the metal/oxide/electrolyte interface; first  $Al^+$  ions are formed at the metal/oxide interface, and then migrate through the oxide/solution interface where they are oxidized to  $Al^{3+}$ . In acid medium, all processes are merged in one loop, and this could be explained based on domination of the first capacitive loop [47]. An equivalent circuit of elements depicted in Fig. 3C for the EIS obtained in HCl, and another one shown in Fig. 3D for EIS obtained in NaOH are shown. In this equivalent circuit,  $R_s$  is the solution resistance,  $R_{ct}$  is the charge transfer resistance (where RL and L represent the inductive elements). Regarding Chi squared values used for fitting impedance results, the Chi squared was <0.001.

### 3.4. Adsorption isotherm

Studying the adsorption mode is critically important as it is related to the nature of the components included in this process, i.e., metal, electrolyte and the inhibitor [48–50]. The adsorption of inhibitor molecules in aqueous media occurs via a quasi-alternative operation in which adsorbed water molecules are substituted by additive molecules. This adsorption hinders the corrosion reaction of the metal in the corrosive medium. Here, it is believed that the degree of surface coverage ( $\theta$ ) is the determining factor that reflects the inhibition efficiency, and it is estimated as cited in the experimental section. Among several isotherms, exper-

imental results fitted well with Langmuir one which is represented as follows;

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh} \quad (2)$$

where,  $C_{inh}$  is the concentration of SIL and  $K_{ads}$  is the adsorption process' equilibrium constant. A straight line (data are not shown) with high correlation coefficient is obtained in both cases, regression equations: ( $Y = 0.986X + 10^{-5}$ ) and ( $Y = 0.971X + 2*10^{-5}$ ) in HCl and NaOH, respectively. The slope values are approximately equal to one confirming that the adsorption of the inhibitor obeys the Langmuir isotherm. This indicates that a monolayer is formed without interaction between adsorbed species. From the intercept, the values of  $K_{ads}$  were computed and was found to equal  $10^5$  and  $5 \times 10^4$  in HCl and NaOH, respectively. This large value indicates an efficient adsorption and hence higher inhibition efficiency. From the values of  $K_{ads}$ , the standard free energy for adsorption ( $\Delta G^\circ_{ads}$ ) using the following equation;

$$K_{ads} = 1/55.5 \exp(-\Delta G^\circ_{ads}/RT) \quad (11)$$

where 55.5 is the concentration of  $H_2O$ ,  $T$  is the temperature, and  $R$  is the gas constant. The free energy of adsorption was found to equal  $-39.12$  and  $-34.6$  kJ/mol, in HCl and NaOH, respectively. These values are in-between the two types of adsorption, signaling a mixed mode of adsorption, i.e., chemical mode preceded by a physical one.

The apparent activation energy ( $E_a$ ) has been determined by applying the Arrhenius relationship:

$$\log(CR) = \frac{-E_a}{(2.303RT)} + \log A \quad (3)$$

where  $R$  is the gas constant,  $T$  is the absolute temperature (K) and  $A$  is the Arrhenius pre-exponential factor. Fig. 4A presents the Arrhenius plot based on the above equation for the corrosion of 6063 AA in HCl solutions both in the absence and presence of  $5 \times 10^{-4}$  M SIL. Similar curves were obtained in the case of free 1.0 M NaOH in the devoid of and containing various concentrations of SIL but not visible. The activation energy was computed utilizing the expression

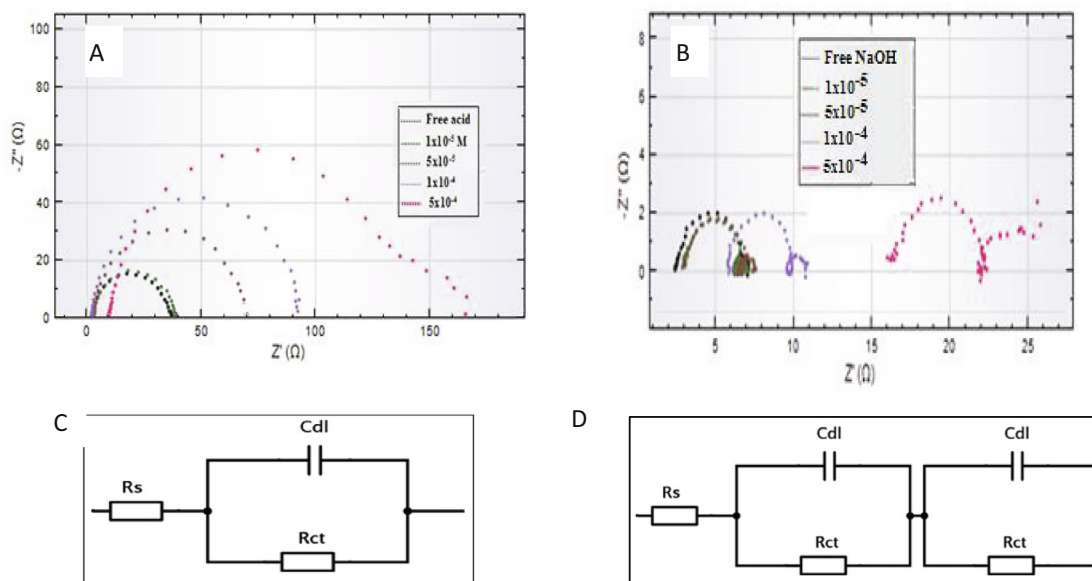
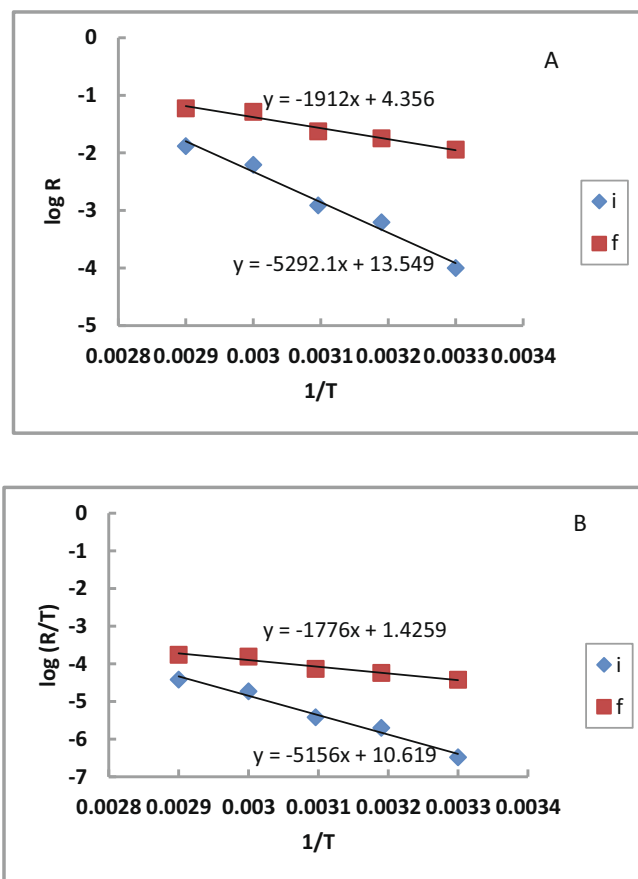


Fig. 3. Nyquist plots for 6063 AA in free A) 1.0 M HCl and B) 1.0 M NaOH solutions containing various concentrations of SIL drug. (C and D) the Randles circuit for the studied system in 1.0 M HCl and 1.0 M NaOH, respectively.





**Fig. 4.** (A) Arrhenius plot ( $\log CR$  versus  $1000/T$ ) for 6063AA in free 1.0 M HCl solutions containing various concentrations of SIL drug f) Blank solution i) Inhibited solution. (B) Transition state plots of  $\log CR/T$  versus  $1000/T$  for obtained at 6063AA in free 1.0 M HCl solutions containing various concentrations of SIL drug f) Blank solution i) Inhibited solution.

**Table 2**

Thermodynamic activation parameters for corrosion of 6063AA in blank 1.0 M HCl and 1.0 M NaOH solutions and including 0.0005 M of SIL.

Solution	$E_a$ ( $\text{kJ}\cdot\text{mol}^{-1}$ )	$\Delta H^*$ ( $\text{kJ}\cdot\text{mol}^{-1}$ )	$-\Delta S^*$ ( $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ )
Free 1.0 M HCl	7.60	5.02	30.19
1.0 M HCl + $5 \times 10^{-4}$ M SIL	120.17	117.57	9.67
Free 1.0 M NaOH	36.60	34.00	20.50
1.0 M NaOH + $5 \times 10^{-4}$ M SIL	101.07	98.72	6.20

$E_a = -(\text{slope}) \times 2.303R$ , see Table 2. From this table, it is apparent that, the presence of the SIL drug increases the values of  $E_a$  and thus reduces the corrosion rate of the 6063AA. These data indicate that the examined SIL drug acts as inhibitor by increasing the  $E_a$  of the corrosion 6063AA by setting up a barrier to mass and charge transfer by its adsorption onto the 6063AA surface.

The values of standard enthalpy ( $\Delta H^*$ ) and entropy of activation ( $\Delta S^*$ ) was determined by applying the transition state equation [51,52]:

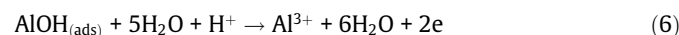
$$CR = \frac{RT}{Nh} \exp\left(\frac{\Delta S}{R}\right) \exp\left(-\frac{\Delta H}{RT}\right) \quad (4)$$

where,  $h$  is Planck's constant and  $N$  is the Avogadro number, respectively. A plot of  $\log (CR/T)$  against  $1/T$  (Fig. 4a, b) gave straight lines with a slope of  $-\Delta H^*/2.303R$  free 1.0 M NaOH in the devoid of and

containing various concentrations of SIL but not visible. The activation thermodynamic parameters  $\Delta H^*$  and  $\Delta S^*$  were computed, as recorded in Table 2. The positive signs of  $\Delta H^*$  denotes that the corrosion of 6063 AA is of endothermic nature. The values of  $\Delta H^*$  in the acid medium differ from those in alkali medium, which means that the type of aggressive solutions affects its adsorption strength on the metal surface. The negative value of  $\Delta S^*$  for both the free acid and alkaline media and those containing SIL drug signalizes that the formation of the activated complex represents a correlation instead of a disintegrating step, which means a decrease in turbulence happen during the course of the transition path from the reactants to the activated complex.

### 3.5. Interpretation of the inhibition process

In acid solution aluminum dissolution is supposed to follow the following mechanism forming a soluble complex [53];



In the case of NaOH, it has been reported that the corrosion of Al is controlled by the formation of a local cell, i.e., a partial anodic and cathodic reactions occurred on adjacent parts of the electrode. Corrosion is controlled by the prevailing reaction in addition to the native surface oxide film [54]. Thus Al dissolution may follow direct (involves the movement of aluminium ions through the film) or indirect (involves consecutive oxide film formation and dissolution) pathways [55–57]. Some parts of the passive film contains some defects and thus it is relatively more soluble; Al atoms gradually removed via electrochemical oxidation of Al according to the subsequent reaction;



And the subsequent chemical reaction

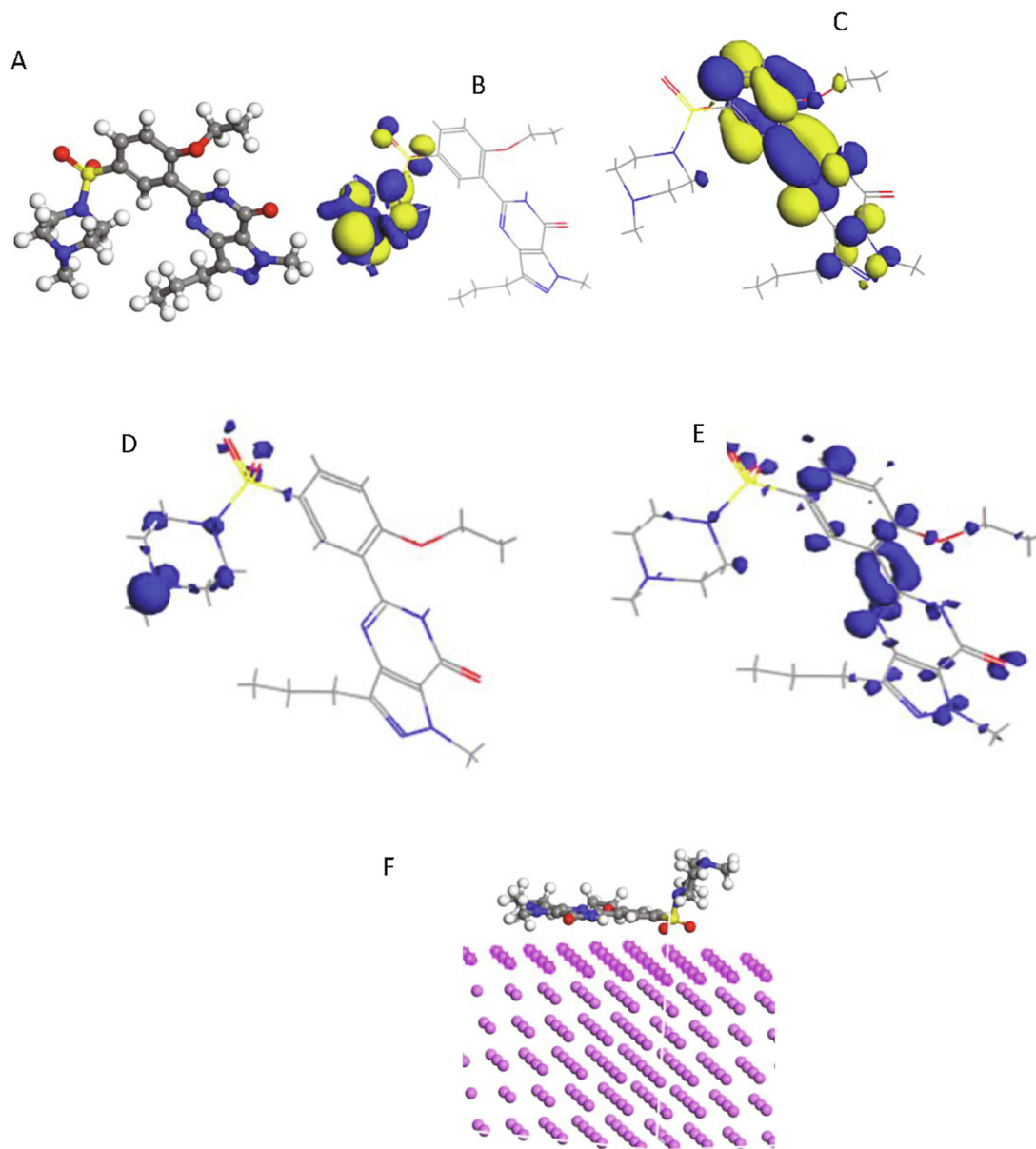


The above electrochemical reaction results in the formation of a soluble aluminate ion,  $\text{Al}(\text{OH})_4^-$  leaving a bare surface site ready for another further dissolution process [58]. The above-mentioned anodic reactions are coupled by the possible following cathodic reaction, with the water reduction is the predominant one [59];



### 3.6. Computational methodology

Sildenafil structure is characterized by four moieties namely, pyrazole, pyrimidinone, phenyl and piperazine (Fig. 5A). Frontier molecule orbital density (FMO)  $E_{\text{HOMO}}$  and  $E_{\text{LUMO}}$  are the parameters used to calculate the energy gap  $\Delta E$ , Global hardness  $\eta$ , global softness  $S$ , ionization potential  $I$ , electron affinity  $A$ , absolute electronegativity  $X$ , global electrophilicity index  $\omega$ , the back donation  $\Delta E_{\text{Back-donation}}$ , the binding energy  $E_{\text{BE}}$ . Geometry optimization on this molecule was applied using DMol3 calculation Model included in Materials Studio v7.0. Electronic parameters were; restricted Spin polarization, Zero Charge, Functional pwc. All electrons in core treatment are considered, DNP Basis set". Both  $E_{\text{HOMO}}$  and  $E_{\text{LUMO}}$ ; were determined as registered in Table 3 and graphically given



**Fig. 5.** (A) Sildenafil: Colors; red, blue, grey and white for Oxygen, Nitrogen, Carbon and Hydrogen, respectively, (B and C) Graphical representation of (B) HOMO, and (C) LUMO of Sildenafil, (D, E) Graphical representation of Fukui functions of Sildenafil; (D)  $f^-$  and (E)  $f^+$ , (F) Adsorption configuration at equilibrium of Sildenafil on Al (111) obtained by molecular dynamic simulation.

**Table 3**  
Quantum chemical descriptors of Sildenafil.

High occupied molecular orbital (eV)	$E_{\text{HOMO}}$	-5.170
Low unoccupied molecular orbital (eV)	$E_{\text{LUMO}}$	-4.163
Energy gap (eV)	$\Delta E$ $\Delta E_{\text{gap}} = E_{\text{LUMO}} - E_{\text{HOMO}}$	1.004
Ionization potential (eV)	$I = -E_{\text{HOMO}}$	5.170
Electron affinity (eV)	$A = -E_{\text{LUMO}}$	4.163
Absolute electronegativity (eV)	$X = (I + A)/2$	4.667
Global hardness (eV)	$\eta = (I - A)/2$	2.010
Global softness (eV) <sup>-1</sup>	$S = 1/\eta$	368.338
Global electrophilicity index (eV)	$\omega = \mu^2/2\eta$ , where $\mu = -X$	10.780
Back-donation Energy (eV)	$\Delta E_{\text{Back-donation}} = h/4$	0.503
The fraction of electron transferred	$\Delta N = \frac{X_{\text{Fe}} + X_{\text{Inh}}}{2(\eta_{\text{Fe}} + \eta_{\text{Inh}})}$	4.620
$E_{\text{BE}}^{\text{M}}$ k Cal/mol	$= (E_{\text{M}} + E_{\text{Inh}}) - E_{\text{Inh+M}}$	-113.445

in Fig. 5B and C. The following parameters are calculated using equations represented in previous studies [60–66]  $I$ ,  $A$ ,  $\chi$  and  $\eta$  can be studied in terms of the  $E_{\text{HOMO}}$  and the  $E_{\text{LUMO}}$ . As well as, Fukui indices ( $f^+$  and  $f^-$ ) which represent local nucleophilic and electrophilic attacks from DMol3 calculation First, Sildenafil molecule was optimized using Forcite Model. To determine the location of Sildenafil and interaction model with Al cell using following steps: first, cleaving the surface along (111) plane and relaxing the surface. Second, building the 2D surface into a super cell (10:10) containing the Al surface. The molecular dynamic simulation for Al (111) surface was carried out with periodic boundary (Lattice parameter A:  $14.3 \times 14.3 \times 21.6 \text{ \AA}$ ). Third, adding a vacuum slab above the Al to build a 3D cell, and setting the vacuum thickness as 20 Å; The adsorption locator module has been applied to the title Al (111) system to calculate binding energy between Sildenafil and Al (111) surface as follows:

$$E_{\text{BE}}(\text{kcal/mol}) = (E_{\text{M}} + E_{\text{Inh}}) - E_{\text{Inh+M}} \quad (13)$$

where the binding energy is  $E_{BE}$ , the total energy of metal crystal is  $E_M$  and is the total energy of Sildenafil molecule is  $E_{Inh}$  and the energy of the two merged investigated molecules with Al is  $E_{Inh+M}$ .

### 3.7. Theoretical studies

Frontier molecule orbital density (FMO) distributions of Sildenafil are represented in Fig. 5D and E. The electron density of  $E_{HOMO}$  is shown to be distributed over piperazine and  $SO_2$  moieties. It indicates that piperazine moiety tends to donate electrons to lower empty molecular orbital energy. However,  $E_{LUMO}$  is distributed over Pyrazole, pyrimidinone and phenyl moieties which are responsible for accepting electrons from the d orbital of the metal.

Smaller values of ionization potential (I) and global hardness ( $\eta$ ) point to the ease of electron donation, as the higher value of global softness does. Electron transfer  $\Delta N$  occurs once an electron exchanges from an atom or a molecule to another chemical structure which is commonly involve transition metal complex. The electronic flow happens from lower electronegativity Sildenafil to higher value Al surfaces. So, the  $\Delta N$  from Sildenafil molecule to the atoms of metal was evaluated. In this study, the electronegativity of bulk aluminum was used  $\chi_{Al} = 1.61$  eV based on Pauling scale and a global hardness of  $\eta_{AA} = 0$ , by assuming that for a metallic bulk  $I = A$ . Condensed Fukui functions shown in Fig. 5 allow us to illustrate each part of Sildenafil molecule. It is evident that pyrazole, pyrimidinone and phenyl moieties are responsible for the nucleophilic  $f^-$ , however, the electrophilic  $f^+$  attack due to piperazine moiety. The most stable Sildenafil conformation adsorbed on Al (111) as illustrated in Fig. 5F was generated by adsorption locator model. The obtained adsorption energy of the investigated molecule on Al cell is  $-113.445$  k Cal/mol. It is observed that the adsorbed moieties are pyrazole, pyrimidinone and phenyl moieties which they are responsible for electron transfer between Sildenafil and Al(111) surface.

### 3.8. Correlation of experimental results with quantum calculations

5. The quantum chemical calculation is dependent on the molecular structure, and could predict a suitable corrosion inhibitor with high efficiency. The parameters related to the inhibition effect of an inhibitor are the energy of the highest occupied ( $E_{HOMO}$ ) and lowest unoccupied ( $E_{LUMO}$ ) molecular orbitals, energy gap ( $\Delta E_{Gap}$ ), and the fraction of electron transferred  $\Delta N$ . Such parameters can be utilized to understand the adsorption phenomenon of the SIL drug on the electrode surface. Recall Table 3, the  $E_{HOMO}$  and  $E_{LUMO}$  values refer to the density of electrons spread across the entire molecule. The atoms and  $\pi$  system are mainly responsible for the interaction with the metal surface [67]. The value of  $E_{HOMO}$  points to the electron donation tendency of the SIL molecule to the corroding metal. The value of  $E_{LUMO}$ , elucidates the affinity of the SIL to accept electrons. In addition, the larger value of  $\Delta N$  ( $\Delta N > 0$ ) indicates the affinity of the transfer of electron from SIL molecule to the 6063AA surface.

## 4. Conclusions

The effect of Sildenafil (SIL) on the corrosion behavior of 6063Al in HCl and NaOH was inspected. Weight loss and polarization and impedimetric measurements revealed that SIL is an efficient corrosion inhibitor in HCl and NaOH solutions. The inhibitory action of the SIL depends on the type aggressive media, the concentration of SIL drug, the temperature and the exposure time as an important step in protecting of 6063Al against corrosion. The adsorption of the SIL drug on the 6063Al surface obeyed the Langmuir isotherm. SIL drug acts as a mixed inhibitor in acidic and alkaline media. The

quantum chemical calculations supported the experimental results.

### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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